

Local correlations, non-local screening, multiplets, and band formation in NiO

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Abstract. We report on a comparative study of the valence band electronic structure of NiO as bulk material and of NiO as impurity in MgO. From the impurity we have been able to determine reliably the parameters which describe the local correlations, thereby establishing the compensated-spin character of the first ionization state or the state created by hole doping. Using bulk-sensitive x-ray photoemission we identify pronounced satellite features in the valence band of bulk NiO which cannot be explained by single-site many body approaches nor by mean field calculations. We infer the presence of screening processes involving local quasi-core states in the valence band and non-local coherent many body states. These processes are strong and the propagation of an extra hole in the valence band of NiO will therefore be accompanied by a range of high energy excitations. This in turn will make the observation of the dispersion relations in the Ni 3d bands difficult, also because the effective band width is no more than 0.25 eV as estimated from multi-site calculations.

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NiO is a benchmark system in solid state physics. It crystallizes in the NaCl structure, has a partially filled $3d$ shell ($\text{Ni}^{2+} d^8$), and is an antiferromagnetic insulator with a Néel temperature of 523 K [1]. It was pointed out early on by de Boer and Verwey [2] that many of the properties of the $3d$ transition metal compounds do not agree with the predictions of band theory, e.g., standard band theory predicts NiO to be metallic. A qualitative explanation was proposed in terms of the Mott-Hubbard model [3, 4] in which the on-site Ni $3d$ - $3d$ Coulomb interaction plays a decisive role.

An early *ab initio* attempt to fix the shortcoming of band theory was to treat NiO as a Slater insulator in which the doubling of the unit cell allows for the existence of a gap [5, 6, 7]. However, the calculated gap of about 0.2 eV [5] turned out to be much too small: A combined photoemission (PES) and bremsstrahlung-isochromat (BIS) spectroscopy study showed that the band gap is 4.3 eV [8] and established thereby the correlated nature of NiO. The inclusion of a self-interaction-correction (SIC) or Hubbard U term to the density-functional formalism may provide a justification for the magnitude of the experimental band gap [9, 10].

Yet, one of the most direct methods to critically test the accuracy of the different approaches, is to determine the excitation spectrum associated with the introduction of an extra particle into the system [13]. Curve (a) in Fig. 1 displays the valence band x-ray photoemission spectrum (XPS, $h\nu = 1486.6$ eV) of an *in situ* cleaved NiO single crystal. This spectrum represents essentially the Ni $3d$ spectral weight since the photoionization cross section of the O $2p$ is relatively small [14]. One can clearly observe from curve (e) in Fig. 1 that the Ni $3d$ density of states calculated by band theory (in the local density approximation, LDA) does not match at all: It has a Fermi cut-off and the line shape is completely different. The inclusion of the Hubbard U in the calculations (LDA+ U) does not solve the line shape problem, see curve (d). All this demonstrates the shortcomings of mean field theories to describe spectra associated with the fundamental one-particle Green's function of the system [10, 15].

A completely different approach is to give up the translational symmetry of the system in order to focus on the local correlations and, especially, the dynamics of the propagation of the injected particle. Curve (c) of Fig. 1 shows the Ni $3d$ spectral weight from an early cluster configuration-interaction calculation by Fujimori and Minami [12], which also includes the full atomic multiplet theory. The agreement with the experimental spectrum is extremely good. Nevertheless, a later cluster calculation by van Elp *et al.* [11] arrived at a less satisfactory result: Peak B has almost disappeared in the calculation, see curve (b). The prime motivation to use a different set of model parameters here is to infer that the first ionization state is low spin (2E) [16] rather than the Hund's rule high spin (4T), analogous to the case of Zhang-Rice singlets in the cuprates [17, 18]. Recent developments combining LDA with dynamical mean field [19, 20, 21, 22] or GW approaches [23] yield Ni $3d$ spectral weights which deviate in important details from the experimental spectrum. These discrepancies between the experiment and the later theoretical simulations [11, 19, 20, 21, 22] do not provide confidence that one has made progress in understanding the nature of the first ionization state.

The issues that we need to address now are threefold. First of all we have to establish whether the XPS valence band spectrum in Fig. 1 is truly representative for bulk NiO. There are reports in the literature claiming that certain satellite peaks in the Ni $2p$ spectrum are due to surface effects [24, 25, 26, 27]. Second, we have to determine to what extent a single-site many body approach can be utilized to

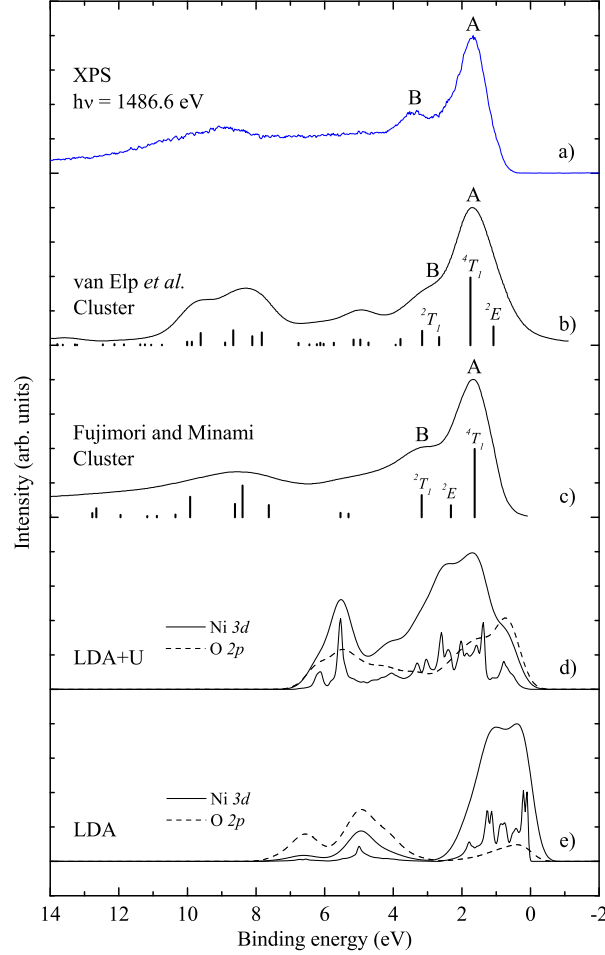


Figure 1. (Color online) Valence band XPS (1486.6 eV) spectrum of an *in situ* cleaved NiO single crystal. The results of two single-site cluster calculations (reproduced from Refs. [11] and [12]), and LDA and LDA+U calculations are also included for comparison.

describe the electronic structure of NiO for which band formation is also essential. Third, we need to identify the nature of the first ionization state in the framework of a local *ansatz*. To this end we measured the valence band of NiO utilizing the more bulk-sensitive hard x-ray photoelectron spectroscopy (HAXPES) and we investigated experimentally the electronic structure of NiO impurities in MgO.

The XPS data ($h\nu = 1486.6$ eV) on *in situ* cleaved NiO single crystals were recorded using a Vacuum Generators twin crystal monochromator Al- $K\alpha$ source and an Scienta SES-100 analyzer, with an overall energy resolution set to 0.35 eV. The HAXPES data ($h\nu = 6500$ eV) were taken at the Taiwan beamline BL12XU of SPring-8 in Hyogo, Japan using an MBS A-1HE analyzer. The overall energy resolution was set to 0.35 eV. The NiO impurity in MgO system was prepared *in situ* as 10-20 nm thin films on polycrystalline Ag by means of molecular beam epitaxy. The measurements were performed at the 11A1 Dragon beamline of the NSRRC in Hsinchu, Taiwan. The

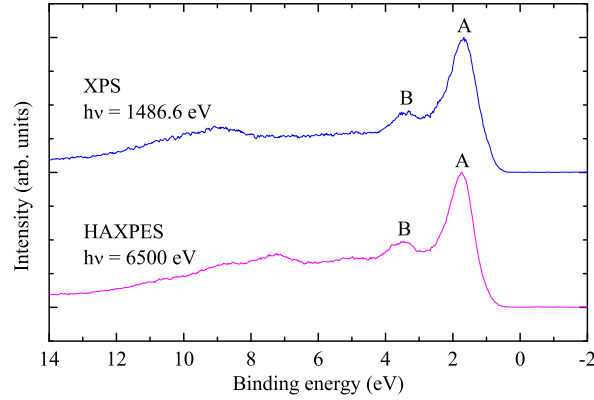


Figure 2. (Color online) Valence band photoemission spectra of an *in situ* cleaved NiO single crystal recorded using 1486.6 eV (XPS) and 6500 eV (HAXPES) photons.

photoemission spectra were recorded at the Cooper minimum of Ag 4d ($h\nu = 140$ eV) [28] using a Scienta SES-100 analyzer with an overall energy resolution set at about 0.15 eV.

In Fig. 2 we show the valence band photoemission spectra of a freshly cleaved NiO bulk crystal, taken with a photon energy of 1486.6 eV (XPS) and 6500 eV (HAXPES). By increasing the photon energy we increase also the kinetic energy of the outgoing photoelectron and, thus, also the inelastic mean free path. One can estimate that the probing depth is then enhanced from about 15 Å to roughly 80 Å [29]. We observe that the spectra are very similar. We, thus, conclude that the XPS data as displayed in Figs. 1 and 2 is representative for the NiO bulk material and that the contribution of surface effects [24, 25, 26, 27] can be safely neglected. To be specific: Peak B is intrinsic for bulk NiO. We would like to note that increasing the photon energy from 1486.6 eV to 6500 eV does not alter much the Ni 3d character of the spectrum. The O 2p photoionization cross section relative to that of the Ni 3d remains very small, it changes from 1/13 to only 1/10 [14], meaning that peak B truly belongs to the Ni 3d spectral weight and not to the O 2p [21].

The valence band spectrum of the $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ impurity system is shown in Fig. 3 together with the spectrum of an MgO reference thin film grown simultaneously under identical oxygen and substrate conditions. The $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ film (and also the MgO film) was capped by 2 monolayers of MgO in order to prevent the surface termination to have an effect on the local electronic structure of the Ni impurity. The inset in the figure displays the Ni $L_{2,3}$ x-ray absorption spectra of the $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ and the NiO bulk. The spectra are essentially identical, verifying that the Ni in the $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ has very similar local surrounding (NiO_6 octahedra) as in the bulk.

The valence band spectra of the $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ and MgO systems are normalized to their O 2s core level intensities. Both are dominated by the O 2p valence band, yet, there are clear differences between them due to the presence or absence of the 5% NiO impurity. The difference spectrum multiplied by a factor of 6 is given by the red curve in Fig. 3. The line shape remains the same for films with lower Ni concentrations, as is the case for that of the Ni 2p [30]. This curve represents essentially the Ni 3d spectral weight of the NiO impurity since the photoionization cross section of the Ni

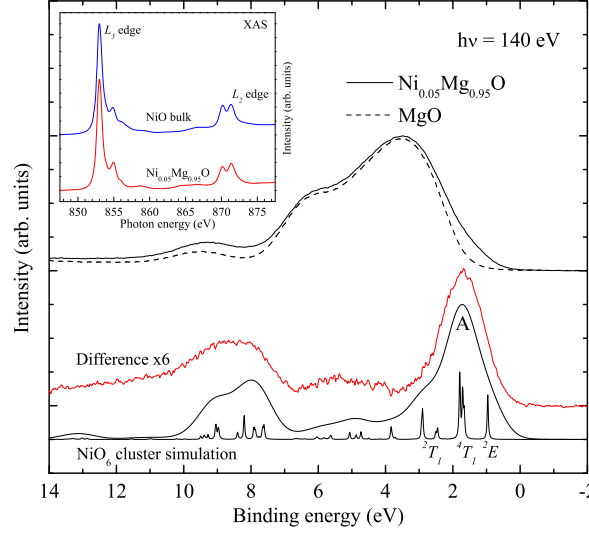


Figure 3. (Color online) Extraction of the NiO impurity valence band photoemission spectrum: Valence band spectra of $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ and an MgO reference, together with the resulting difference spectrum. Also included is the result of a single-site NiO_6 configuration-interaction cluster calculation. The inset shows the Ni $L_{2,3}$ x-ray absorption spectrum of the $\text{Ni}_{0.05}\text{Mg}_{0.95}\text{O}$ together with that of bulk NiO.

$3d$ is an order of magnitude larger than that of the O $2p$ at the photon energy used [14]. Remarkable is that it is different from the spectrum of bulk NiO as shown in Figs. 1 and 2. The impurity spectrum lacks specifically peak B which is prominently present in the bulk spectrum.

To interpret and understand the impurity spectrum, we have performed simulations using the well-proven configuration-interaction cluster model which includes the full atomic multiplet theory [31, 32, 33]. The simulations have been carried out for a NiO_6 cluster using the program XTLS 8.3 [31].

The bottom curve in Fig. 3 shows the Ni $3d$ one-electron removal spectrum from the cluster calculation. The agreement with the experiment is very satisfactory. In order to achieve this, we have started the calculations by using parameter values which were suggested from earlier studies on NiO [11, 31, 34, 35]. We then fine-tune the parameters describing the octahedral crystal and ligand fields, and also the difference between the Hubbard U and the O $2p$ -Ni $3d$ charge transfer energy [36]. The crucial issue here is to obtain a main line (peak A) without having another feature appearing at about 2 eV higher energies (peak B) as was the case in the simulations by Fujimori and Minami [12] and by van Elp *et al.* [11]. This has implications for the energetics of the states making up the valence band as we explain in the following.

A detailed look at the cluster calculations displayed in Fig. 1 shows that peak A is given by the 4T_1 final state of the Ni $3d^7$ multiplet structure while peak B is due to the 2T_1 . Avoiding the appearance of peak B means that the energy splitting between these two states must be made smaller, e.g., 1 eV or less. This is what we have done in our simulation in Fig. 3, using different but equally reasonable parameter values [36]. The consequences for the physics are, yet, quite far reaching. Given the fact that various x-ray absorption studies find an effective octahedral crystal and ligand field

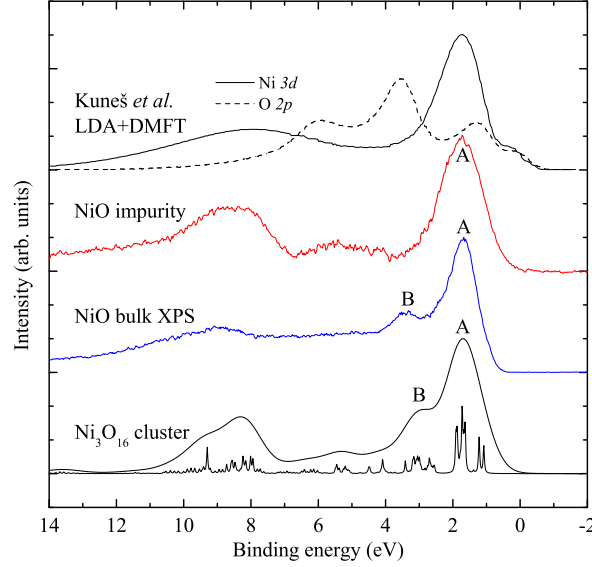


Figure 4. (Color online) Comparison of the valence band photoemission spectra of bulk NiO and NiO impurity in MgO. Also included is the simulated Ni 3d and O 2p spectral weights of the NiO valence band from a LDA+DMFT calculation (reproduced from Ref. [21]) and the result of a three-site Ni_3O_{16} configuration-interaction cluster calculation.

splitting of about 1.65 eV [34, 35], i.e., the splitting between the isospin 2T_1 and 2E states, we arrive at the conclusion that the 2E must be lower in energy than the 4T_1 by 0.65 eV or more. This is what we read from our results in Fig. 3. In other words, our impurity study provides the spectroscopic evidence that the first ionization state has a compensated-spin character rather than the Hund's rule high-spin. This in turn justifies that the ground state of a hole doped NiO system may indeed be low-spin in nature [16].

We now return to the problem of the bulk NiO valence band spectrum. Fig. 4 shows the Ni 3d spectral weight taken with XPS and compares it with the spectra of the NiO impurity and of the single-site LDA+DMFT calculation [21]. One can clearly observe that peak B is absent in the impurity as well as in the Ni 3d spectral weight of the single-site calculation. In fact, one could infer that the calculation reproduces quite well the impurity spectrum, with perhaps some discrepancies due to the incomplete implementation of the multiplet structure of the on-site Coulomb interactions. Yet, the discrepancy with the bulk spectrum strongly suggests that the origin of peak B must be sought in non-local correlations, i.e., effects which cannot be included in a single-site approach.

Our suggestion is that peak B is due to non-local screening processes involving the formation of low-energetic coherent many body states on neighboring NiO clusters, which are of the 2E type as we have shown above. The mechanism is analogous as proposed earlier for the Ni 2p core level spectrum of bulk NiO [37], but the application of it for the valence band is only valid for local states which are relatively stable against band formation. This may not be applicable for the 2E state, which is a state in which a hole is injected in an e_g orbital starting from the $3d^8\ ^3A_2$ ground state [35]. This hole can be expected to readily propagate in the lattice since the hopping between the

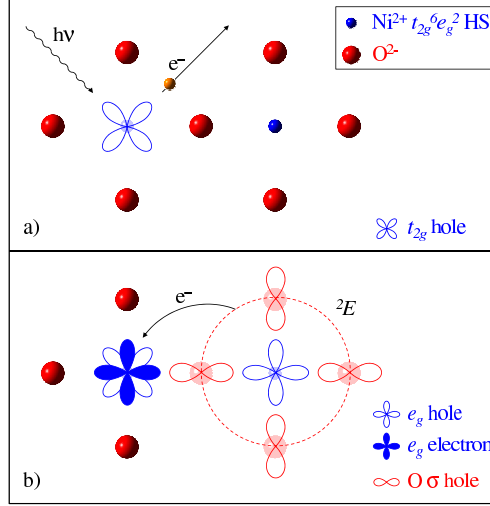


Figure 5. (Color online) Non-local screening in valence band photoemission on NiO: (a) Creation of the atomic-like (quasi-core) 4T_1 hole state by the photoemission process. (b) Screening by a next nearest neighbor NiO_6 cluster producing a coherent low-energetic 2E hole state there.

$\text{Ni } 3d(e_g)$ and $\text{O } 2p(\sigma)$ orbitals are rather large [11, 37], yet, it may leave behind an energetically costly wake of wrong spins in the antiferromagnetic lattice. In any case, it would not be meaningful to describe its band formation as a low-energy screening process involving neighboring 2E states [38].

However, for the main peak of the bulk NiO spectrum, i.e., the 4T_1 state, we infer that we can make a meaningful approximation by using the coherent 2E screening model. The 4T_1 consists of a hole injected into the t_{2g} orbital, and its ability to move is rather limited since the overlap between the $\text{Ni } 3d(t_{2g})$ and $\text{O } 2p(\pi)$ is small. One could consider the 4T_1 as a localized quasi-core state. We then can invoke the non-local screening process as follows: After the creation of the 4T_1 state, an e_g electron from a neighboring NiO cluster hops onto the Ni site, leaving behind a coherent 2E hole state on that neighbor. A sketch for this process is given in Fig. 5. These two states are energetically almost degenerate [37], and the $\text{Ni } 3d(e_g)$ and $\text{O } 2p(\sigma)$ hybridization between them is then strong enough to produce two peaks: Not only the main peak A but also the satellite peak B.

To confirm our assignments, we have performed a Ni_3O_{16} cluster calculation consisting of three edge-shared NiO_6 octahedra. While all the $\text{O } 2p$ and $\text{Ni } 3d$ orbitals are included for the NiO_6 octahedron in the center where the photo-excitation takes place, those on the other parts of the cluster are replaced by a reduced basis set using the method in Ref. [39]. The results are displayed in Fig. 4 and demonstrate the presence of both peaks A and B. Note that we have used the same parameters as for the single-site calculation which produces only peak A, see Fig. 3. We also note that the energy difference between peaks A and B is somewhat smaller and the intensity of peak B is slightly larger than those of the experiments. This can be explained by the fact that the number of neighboring Ni sites is only two in the Ni_3O_{16} cluster: the energy difference will increase and the intensity of peak B will decrease for a larger number of neighboring sites [39].

To summarize: We have succeeded to determine reliably the Ni 3d valence band spectra representative for bulk NiO as well as for NiO as an impurity system. From the impurity data we are able to extract the local electronic structure and the correlations herein, thereby establishing firmly the compensated-spin character of the first ionization state. By comparing the bulk with the impurity system, we were able to identify features in the bulk NiO spectrum which are caused by screening processes involving local quasi-core valence band states and non-local low-energetic many body states. These processes are strong and cause considerable redistribution of the spectral weight when an extra hole is injected into NiO. This explains why fine features related to the dispersion of the Ni 3d band is difficult to detect [40], also since the effective band width is only of order 0.25 eV as estimated from our multi-site cluster calculations.

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References

- [1] W. L. Roth. Magnetic structures of MnO, FeO, CoO, and NiO. *Phys. Rev.*, 110(6):1333–1341, Jun 1958.
- [2] J. H. de Boer and E. J. W. Verwey. Semi-conductors with partially and with completely filled 3d -lattice bands. *Proc. Phys. Soc. London*, 49(4S):59, 1937.
- [3] N. F. Mott. The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals. *Proc. Phys. Soc. London, Sect. A*, 62(7):416, 1949.
- [4] J. Hubbard. Electron Correlations in Narrow Energy Bands. *Proc. R. Soc. London, Ser. A*, 276(1365):238–257, 1963.
- [5] T. Oguchi et al. Band theory of the magnetic interaction in MnO, MnS, and NiO. *Phys. Rev. B*, 28(11):6443–6452, Dec 1983.
- [6] K. Terakura et al. Transition-Metal Monoxides: Band or Mott Insulators. *Phys. Rev. Lett.*, 52(20):1830–1833, May 1984.
- [7] K. Terakura et al. Band theory of insulating transition-metal monoxides: Band-structure calculations. *Phys. Rev. B*, 30(8):4734–4747, Oct 1984.
- [8] G. A. Sawatzky and J. W. Allen. Magnitude and Origin of the Band Gap in NiO. *Phys. Rev. Lett.*, 53(24):2339–2342, Dec 1984.
- [9] A. Svane and O. Gunnarsson. Transition-metal oxides in the self-interaction-corrected density-functional formalism. *Phys. Rev. Lett.*, 65(9):1148–1151, Aug 1990.
- [10] V. I. Anisimov et al. Band theory and Mott insulators: Hubbard U instead of Stoner I. *Phys. Rev. B*, 44(3):943–954, Jul 1991.
- [11] J. van Elp et al. Electronic structure of Li-doped NiO. *Phys. Rev. B*, 45(4):1612–1622, Jan 1992.
- [12] A. Fujimori and F. Minami. Valence-band photoemission and optical absorption in nickel compounds. *Phys. Rev. B*, 30(2):957–971, Jul 1984.
- [13] C.-O. Almbaldh and L. Hedin. *Handbook on Synchrotron Radiation*, volume 1b. North-Holland, Amsterdam, 1983.
- [14] M. B. Trzhaskovskaya et al. Photoelectron angular distribution parameters for elements $Z = 1$ to $Z = 54$ in the photoelectron energy range 100–5000 eV. *At. Data Nucl. Data Tables*, 77:97, 2001.
- [15] V. I. Anisimov et al. Density-functional theory and NiO photoemission spectra. *Phys. Rev. B*, 48(23):16929–16934, Dec 1993.
- [16] P. Kuiper et al. Character of Holes in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ and Their Magnetic Behavior. *Phys. Rev. Lett.*, 62:221, 1989.
- [17] F. C. Zhang and T. M. Rice. Effective Hamiltonian for the superconducting Cu oxides. *Phys. Rev. B*, 37:3759, 1988.
- [18] H. Eskes and G. A. Sawatzky. Tendency towards Local Spin Compensation of Holes in the High- T_c Copper Compounds. *Phys. Rev. Lett.*, 61:1415, 1988.

- [19] X. Ren et al. LDA+DMFT computation of the electronic spectrum of NiO. *Phys. Rev. B*, 74(19):195114, Nov 2006.
- [20] J. Kuneš et al. NiO: Correlated Band Structure of a Charge-Transfer Insulator. *Phys. Rev. Lett.*, 99(15):156404, Oct 2007.
- [21] J. Kuneš et al. Local correlations and hole doping in NiO: A dynamical mean-field study. *Phys. Rev. B*, 75(16):165115, Apr 2007.
- [22] Q. Yin et al. Calculated Momentum Dependence of Zhang-Rice States in Transition Metal Oxides. *Phys. Rev. Lett.*, 100(6):066406, Feb 2008.
- [23] H. Jiang et al. First-principles modeling of localized d states with the $GW@LDA+U$ approach. *Phys. Rev. B*, 82:045108, 2010.
- [24] L. Sangaletti et al. On the non-local screening mechanisms in the $2p$ photoelectron spectra of NiO and La_2NiO_4 . *Solid State Commun.*, 103(7):421 – 424, 1997.
- [25] L. Soriano et al. Surface effects in the Ni $2p$ x-ray photoemission spectra of NiO. *Phys. Rev. B*, 75(23):233417, Jun 2007.
- [26] I. Preda et al. Interface effects in the Ni $2p$ x-ray photoelectron spectra of NiO thin films grown on oxide substrates. *Phys. Rev. B*, 77(7):075411, Feb 2008.
- [27] R. J. O. Mossaneck et al. Investigation of surface and non-local screening effects in the Ni $2p$ core level photoemission spectra of NiO. *Chem. Phys. Lett.*, 501:437, 2011.
- [28] S. L. Molodtsov et al. Cooper Minima in the Photoemission Spectra of Solids. *Phys. Rev. Lett.*, 85(19):4184–4187, Nov 2000.
- [29] C. J. Powell and A. Jablonski. Evaluation of electron inelastic mean free paths for selected elements and compounds. *Surf. Interface Anal.*, 29:108, 2000.
- [30] S. Altieri et al. Core-level x-ray photoemission on NiO in the impurity limit. *Phys. Rev. B*, 61(20):13403, 2000.
- [31] A. Tanaka and T. Jo. Resonant $3d$, $3p$ and $3s$ Photoemission in Transition Metal Oxides Predicted at $2p$ Threshold. *J. Phys. Soc. Jpn.*, 63:2788, 1994.
- [32] F. M. F. de Groot. X-ray absorption and dichroism of transition metals and their compounds. *J. Electron. Spectrosc. Relat. Phenom.*, 67(4):529 – 622, 1994.
- [33] See the “Theo Thole Memorial Issue”. *J. Electron Spectrosc. Relat. Phenom.*, 86:1, 1997.
- [34] D. Alders et al. Temperature and thickness dependence of magnetic moments in NiO epitaxial films. *Phys. Rev. B*, 57:11623, 1998.
- [35] M. W. Haverkort et al. Magnetic versus crystal-field linear dichroism in NiO thin films. *Phys. Rev. B*, 69:020408, 2004.
- [36] Parameters used for the calculation of the NiO_6 cluster (in eV): $\Delta=5.0$, $U_{dd}=6.5$, $10Dq=0.5$, $T_{pp}=0.8$, $V(e_g)=2.2$, $V(t_{2g})=V(e_g)/2$, ζ see Ref. [31], Slater integrals 70% of Hartree-Fock values.
- [37] M. A. van Veenendaal and G. A. Sawatzky. Nonlocal screening effects in $2p$ x-ray photoemission spectroscopy core-level line shapes of transition metal compounds. *Phys. Rev. Lett.*, 70(16):2459–2462, Apr 1993.
- [38] M. Taguchi et al. Revisiting the Valence-Band and Core-Level Photoemission Spectra of NiO. *Phys. Rev. Lett.*, 100(20):206401, May 2008.
- [39] A. Tanaka. Intersite Effects on Valence Band Photoemission Spectra of Undoped CuO_2 Plane and CuO_3 Chain. *J. Phys. Soc. Jpn.*, 68:3493, 1999.
- [40] Z.-X. Shen, C. K. Shih, O. Jepsen, W. E. Spicer, I. Lindau, and J. W. Allen. Aspects of the correlation effects, antiferromagnetic order, and translational symmetry of the electronic structure of NiO and CoO. *Phys. Rev. Lett.*, 64:2442, 1990.